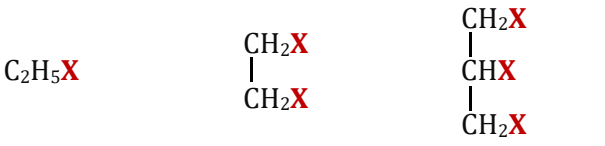
02 Haloalkanes and Haloarenes

The replacement of hydrogen atom(s) in an aliphatic or aromatic hydrocarbon by halogen atom(s) results in the formation of alkyl halide(haloalkane) and aryl halide (haloarenes) respectively.

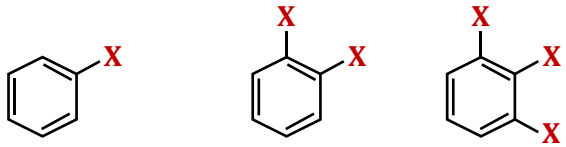
Classification of Haloalkanes and Haloarenes

(a) On the basis of number of halogen(X) atoms:

Haloalkanes and haloarenes may be classified as follows:



Monohaloalkane **Dihaloalkane** **Trihaloalkane**



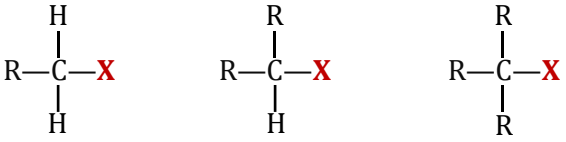
Monohaloarene **Dihaloarene** **Trihaloarene**

Monohalocompounds may further be classified according to the hybridisation of the carbon atom to which the halogen is bonded, as discussed below.

(1) Compounds containing sp^3 C—X bond:

(a) Alkyl halides or haloalkanes

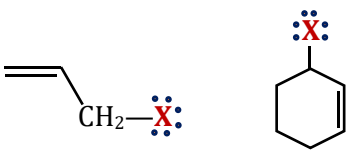
In alkyl halides halogen atom is bonded to an alkyl group.



Primary (1°) **Secondary (2°)** **Tertiary (3°)**

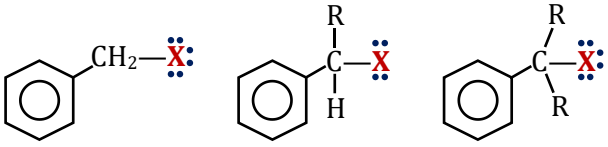
(b) Allylic halides

These are the compounds in which the halogen atom is bonded to an sp^3 hybridised carbon atom next to carbon-carbon double bond.



(c) Benzylic halides

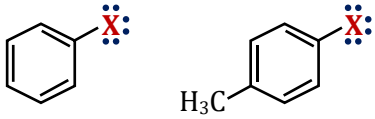
These are the compounds in which the halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring.



(2) Compounds containing sp^2 C—X bond:

(a) Aryl halides or haloarenes

These are the compounds in which the halogen atom is bonded to an sp^2 hybridised carbon atom of an aromatic ring.



(b) Vinylic halides

These are the compounds in which the halogen atom is bonded to an sp^2 hybridised carbon atom of a carbon-carbon double bond.

Methods of Preparation of Haloalkanes

(A) From hydrocarbons:

(a) By halogenation of alkane

$$CH_3—CH_3 + X_2 \xrightarrow{h\nu/\Delta/UV} CH_3CH_2X + HX$$

(b) By hydrohalogenation of alkene

$$CH_3—CH=CH_2 \xrightarrow{HX} CH_3—\underset{\displaystyle X}{\underset{|}{CH}}—CH_3$$

(c) By halogenation of alkene

$$CH_3—CH=CH_2 \xrightarrow[CCl_4]{X_2} CH_3—\underset{\displaystyle X}{\underset{|}{CH}}—\underset{\displaystyle X}{\underset{|}{CH_2}}$$

(B) From alcohol:

$$R—OH + PCl_5 \longrightarrow R—Cl + POCl_3 + HCl$$

$$3R—OH + PX_3 \longrightarrow 3R—X + H_3PO_3$$

$$R—OH + SOCl_2 \longrightarrow R—Cl + SO_2 + HCl$$

$$R—OH + HX \longrightarrow R—X + H_2O$$

(C) Halogen Exchange Reaction:

(a) Finkelstein reaction (Preparation of alkyl iodide)

$$R—X + NaI \xrightarrow[acetone]{dry} R—I + NaX$$

X = Cl, Br

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(b) Swarts reaction (Preparation of alkyl fluoride)

The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3

$CH_3—X + AgF \longrightarrow H_3C—F + AgX$

X = Cl, Br

Physical Properties

Boiling point of Haloalkanes:

Boiling Point $\propto$ Intermolecular force of attraction

$\propto$ Molecular weight

$\propto \frac{1}{\text{Branching}}$ (If molecular weight same)

Due to stronger intermolecular forces of attraction, boiling point of halogen derivatives is more compared to its parent hydrocarbon.

R—H < R—X

Leaving Group

Leaving group is a species that departs with the bonded pair of electrons.

$\overset{\ominus}{Nu} + R—\underset{\text{Leaving group}}{\underline{X}} \longrightarrow R—Nu + \underset{\text{Generally anion}}{\overset{\ominus}{\underline{X}}}$

Leaving group ability $\propto$ Stability of anion

Note: Weaker bases are good leaving group

BEGINNER'S BOX-1

1. Alkyl fluorides are synthesized by
   (1) Finkelstein reaction (2) Swarts reaction
   (3) Kolbe reaction (4) Wurtz reaction
2. Which is Finkelstein reaction ?
   (1) $R–X + NaI \xrightarrow{\text{Acetone}}$ (2) $R–X + AgF \longrightarrow$
   (3) $R–X + NaF \longrightarrow$ (4) $R–F + AgCl \longrightarrow$
3. Which of the following has the highest boiling point ?
   (1) CH_3CH_2I (2) CH_3Cl (3) CH_3I (4) CH_3Br
4. Correct order of leaving group tendency is :-
   (1) $I^\ominus > Br^\ominus > Cl^\ominus > F^\ominus$ (2) $F^\ominus > Cl^\ominus > Br^\ominus > I^\ominus$
   (3) $Cl^\ominus > F^\ominus > Br^\ominus > I^\ominus$ (4) $I^\ominus > Cl^\ominus > Br^\ominus > F^\ominus$
5. Leaving group tendency is maximum in :-
   (1) $CH_3—O^\ominus$ (2) $CH_3–C(=O)–O^\ominus$ (3) $Ph—O^\ominus$ (4) $\overset{\ominus}{C}H_3$
6. Which is best leaving group ?
   (1) $H_3C—O^\theta$ (2) $H_3C–S(=O)_2–O^\ominus$ (3) $H_3C—CH_2^\theta$ (4) $H_3C—NH^\theta$

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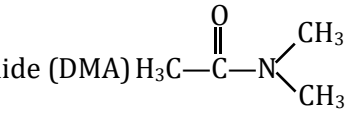
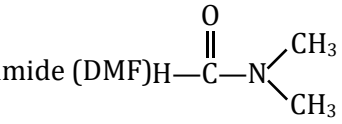
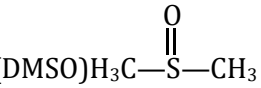
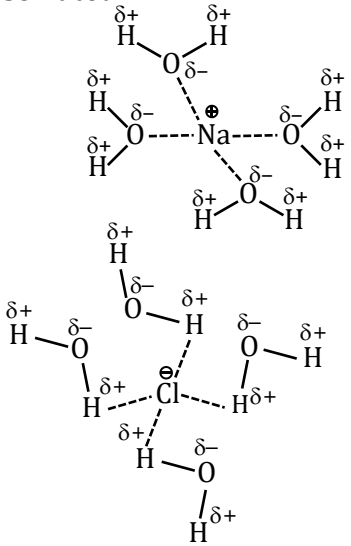
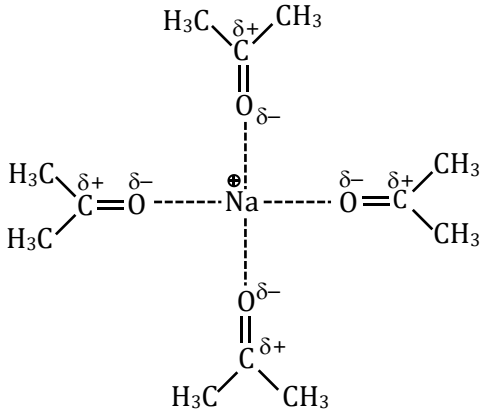
Solvent

Substrate + Reagent $\xrightarrow{\text{Solvent}}$ Product

There are two types of solvents: (1) Polar solvent ($\mu \neq 0$) and (2) Non-polar solvent ($\mu = 0$).

Polar Solvent

Polar Protic Solvent	**Polar Aprotic Solvent**
1. H atom is directly bonded to a more electronegative atom.	**1. H atom is not directly bonded to a more electronegative atom.**
Ex :	**Ex :**
H_2O, ROH, CH_3COOH, NH_3 etc.	N, N-Dimethylacetamide (DMA) 
	N, N-Dimethylformamide (DMF) 
	Acetone
	Dimethyl sulfoxide (DMSO) 
	Ether R—O—R'
2. Both cations and anions are solvated.	**2. Only cations are solvated and not anions. (due to steric crowding)**
	

Non-polar solvent : Neither cation nor anion is solvated. Ex. CCl_4, CS_2 etc.

Nucleophilicity and Basicity

Nucleophilicity is a measure of how fast a nucleophile is able to attack an electrophilic centre. It is a kinetic property.

Basicity is a thermodynamic property.

Note: Stable anion $\Rightarrow$ Weak base or Basicity $\propto \frac{1}{\text{stability of Anion}}$

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Factors affecting nucleophilicity:

1. A negatively charged nucleophile is a better nucleophile than its conjugate acid.

2. Across the period nucleophilicity and basicity order is same

$\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > \overset{\ominus}{O}H > \overset{\ominus}{F}$

3. When the attacking nucleophile is different in size (in a group) then role of solvent (down the group nucleophilicity and basicity order may or may not be same)

Polar protic solvent : $\overset{\ominus}{F} < \overset{\ominus}{Cl} < \overset{\ominus}{Br} < \overset{\ominus}{I}$

Polar aprotic solvent : $\overset{\ominus}{F} > \overset{\ominus}{Cl} > \overset{\ominus}{Br} > \overset{\ominus}{I}$ (No solvation of anion)

Basicity order : $\overset{\ominus}{F} > \overset{\ominus}{Cl} > \overset{\ominus}{Br} > \overset{\ominus}{I}$

Note: If nothing is mentioned consider polar protic solvent.

4. In case of same donor atom, generally nucleophilicity and basicity order is same. (stronger base is stronger nucleophile)

$\overset{\ominus}{O}R > Ph—\overset{\ominus}{O} > R—\overset{O}{\overset{\|}{C}}—\overset{\ominus}{O}$

Chemical Reactions of Haloalkanes

The reactions of haloalkanes may be divided into the following categories:

(i) Nucleophilic Substitution Reaction

(ii) Elimination Reaction

(iii) Reaction with metals

(i) Nucleophilic Substitution Reaction (SN):

$R—X + \overset{\ominus}{N}u \longrightarrow R—Nu + \overset{\ominus}{X}$

Mechanism:

This reaction has been found to proceed by two different mechanisms.

1. S_N1 (Unimolecular Nucleophilic Substitution)
2. S_N2 (Bimolecular Nucleophilic Substitution)

Unimolecular Nucleophilic Substitution (S_N1)

$R—X + \overset{\ominus}{N}u \longrightarrow R—Nu + \overset{\ominus}{X}$

Mechanism:

1st step: $R—X \underset{\text{rds}}{\overset{\text{Slow}}{\rightleftharpoons}} \overset{\oplus}{R} + \overset{\ominus}{X}$

2nd step: $\overset{\oplus}{R} + \overset{\ominus}{N}u \xrightarrow{\text{Fast}} R—Nu$

Characteristics:

1. It is a two step reaction.

2. Kinetics of reaction

Rate = k[alkyl halide] ROR $\propto$ [Alkyl halide]

order = 1

Molecularity = 1

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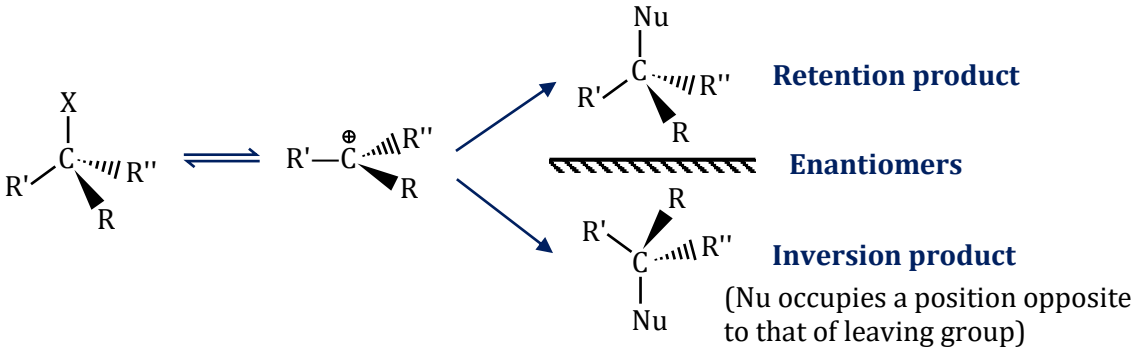
3. Rate is independent of concentration of nucleophile.

4. Carbocation intermediate is formed. Rearrangement may be possible.

5. S_N1 reaction is favoured by polar protic solvent (Ex. H_2O, ROH)

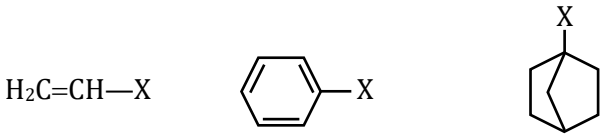
6. Stereochemistry of S_N1 reaction



Note: Theoretically, racemic mixture must be formed but inversion product dominates over retention product. Partial racemisation takes place.

7. Reactivity towards S_N1 reaction $\propto$ Stability of carbocation intermediate

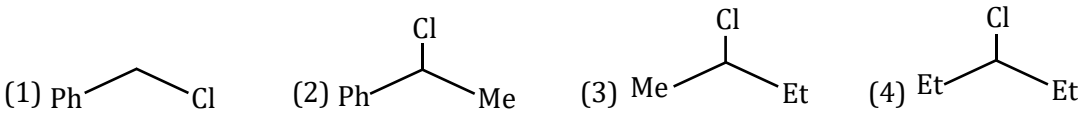
8. S_N1 reaction does not take place in :-



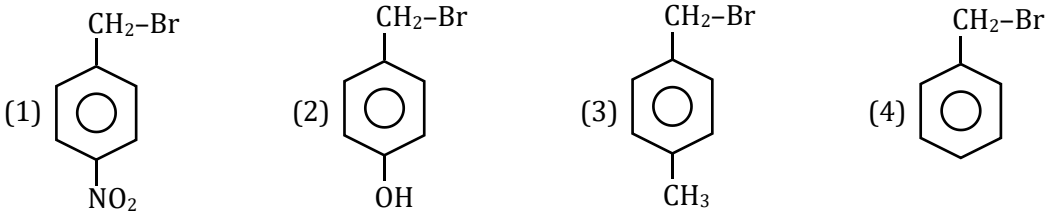
Vinyl halide **Aryl halide** **Bredt's rule violation**

BEGINNER'S BOX-2

1. Which is most reactive for S_N1 reaction :-



2. Which is most reactive for S_N1?



3. In S_N1 the first step involves the formation of
(1) Free radical (2) Carbanion (3) Carbocation (4) None of these

4. Most stable carbocation formed from $(CH_3)_3C–Br$, $(C_6H_5)_3CBr$, $(C_6H_5)_2CHBr$ and $C_6H_5CH_2Br$ would be
(1) $C_6H_5\overset{\oplus}{C}H_2$ (2) $(CH_3)_3\overset{\oplus}{C}$ (3) $(C_6H_5)_3\overset{\oplus}{C}$ (4) $(C_6H_5)_2\overset{\oplus}{C}H$

5. S_N1 reaction on optically active substrates mainly gives
(1) Retention in configuration (2) Inversion in configuration
(3) Racemised product (4) No product

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Bimolecular Nucleophilic Substitution Reaction (S_N2)

$R—X + \overset{\ominus}{N}u \longrightarrow R—Nu + \overset{\ominus}{X}$

Mechanism:

$\overset{\ominus}{N}u + R—X \longrightarrow R—Nu + \overset{\ominus}{X}$

Characteristics:

1. It is a single step reaction.

2. Kinetics of reaction

Rate = k[Alkyl halide][Nucleophile] ROR $\propto$ [Alkyl halide][Nucleophile]

Order = 2

Molecularity = 2

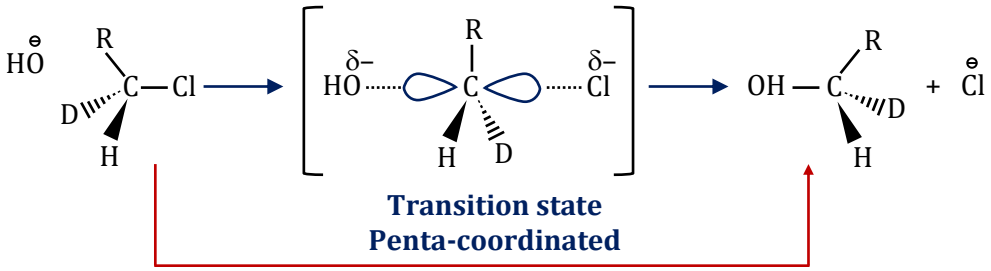
3. Rate is dependent on concentration of nucleophile also.

4. No carbocation intermediate is formed. Hence no rearrangement.

5. S_N2 reaction is favoured by polar aprotic solvent.

(Ex: DMSO, DMF, acetone etc.)

6. Stereochemistry of S_N2 reaction



Transition state
Penta-coordinated

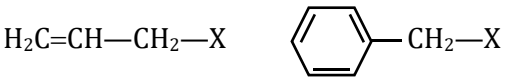
Inversion of configuration (Walden Inversion)

Note: S_N2 reaction completes with 100% inversion of configuration.

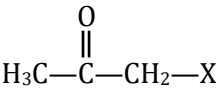
7. Reactivity towards S_N2 reaction $\propto \frac{1}{\text{Steric hindrance}}$

$\propto$ Electrophilicity of carbon attached to halogen.

Note: Allyl and benzyl halide shows S_N2 reaction in good amount.



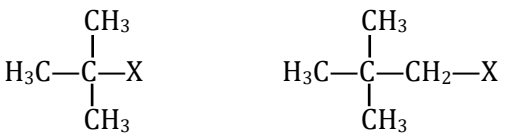
(Allyl halide) **(Benzyl halide)**



shows S_N2 reaction in excellent amount.

8. S_N2 reaction does not take place in :-

Vinyl halide **Aryl halide**



3° alkyl halide **Neopentyl halide** **Bredt's rule violation**

Note: S_N1 and S_N2 reaction does not take place at sp^2 hybridised carbon atom.

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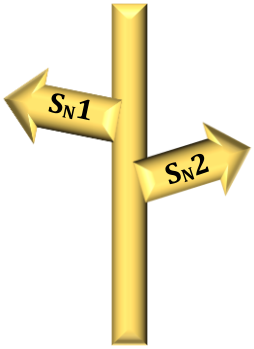
Nucleophilic Substitution Reaction

Generally,

2° alkyl halides

- **S_N1 reaction is favoured by a poor nucleophile (H_2O, ROH)**
- **S_N1 reaction is favoured in polar protic solvent**



- **S_N2 reaction is favoured by high concentration of a good nucleophile (Anionic nucleophiles)**
- **S_N2 reaction is favoured in polar aprotic solvent**

BEGINNER'S BOX-3

1. Which of the following is least reactive towards S_N2 ?

   (1) $(CH_3)_3C-Br$ (2) $Ph-CH_2-Br$ (3) CH_3-Br (4) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-Br$

2. Arrange the following compound in their order of reactivity toward S_N2 reaction :-

   CH_3-F (I) CH_3-Cl (II) CH_3-Br (III) CH_3-I (IV)

   (1) I > II > III > IV (2) IV > III > II > I (3) III > IV > I > II (4) II > III > IV > I

3. Select the correct statement about S_N2 reaction

   (1) Molecularity of reaction is 2

   (2) Order of reaction is 2

   (3) On increasing concentration of nucleophile rate of reaction increases

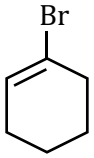
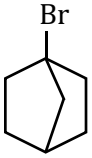
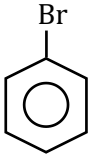
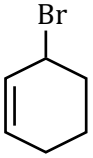
   (4) All of these

4. Which of the following is the correct decreasing order of S_N2 reactivity?

   (1) $R-CH_2-X > R_3CX > R_2CHX$ (2) $R-CH_2X > R_2CHX > R_3CX$

   (3) $R_3CX > R_2CHX > R-CH_2X$ (4) $R_2CHX > R_3CX > R-CH_2X$

5. S_N2 reaction will be negligible in

   (I)  (II)  (III)  (IV) 

   (1) Only IV (2) I, II, III (3) I, III (4) Only II

6. For S_N2 reaction, which is most reactive ?

   (1) $CH_3-CH_2-CH_2-Br$ (2) $CH_3-\overset{\overset{CH_3}{|}}{C}-Br$ (CH_3 below C)

   (3) $CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-Br$ (4) CH_3-CH_2-Br

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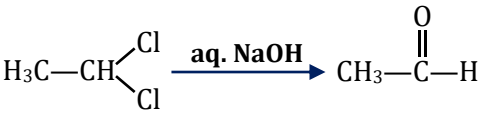
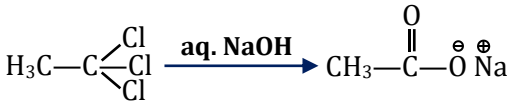
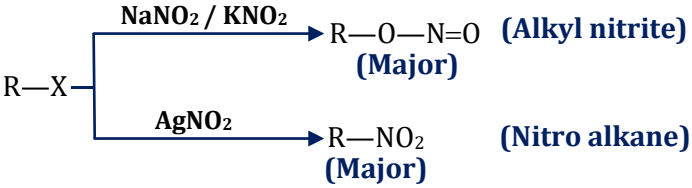
1. Reaction with aq. NaOH / aq. KOH

$CH_3—CH_2—Cl \xrightarrow{\text{aq. NaOH}} CH_3—CH_2—OH$

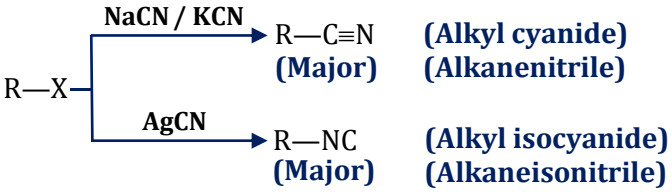




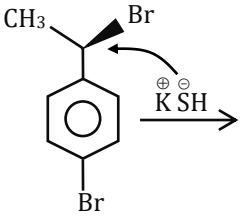
2. Reaction of alkyl halide with $NaNO_2$ / KNO_2 and $AgNO_2$

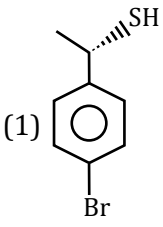


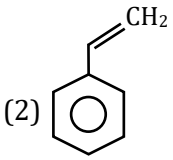
3. Reaction of alkyl halide with NaCN / KCN and AgCN

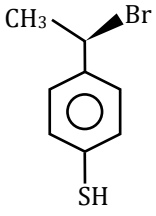


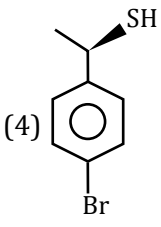
BEGINNER'S BOX-4

1.  (P) ; Major product (P) is :

(1) 

(2) 

(3) 

(4) 

2. Consider the reaction,

$CH_3CH_2CH_2Br + NaOH \longrightarrow CH_3CH_2CH_2OH + NaBr$

This reaction will be fastest in :-

(1) Water (2) Ethanol

(3) Methanol (4) N, N'-dimethylformamide (DMF)

3. $CH_3–CH_2Cl \xrightarrow{AgCN}$ Major product is :

(1) CH_3CH_2CN (2) CH_3CH_2NC (3) $CH_3–CH_3$ (4) $CH_2=CH_2$

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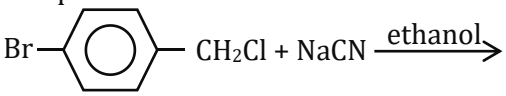
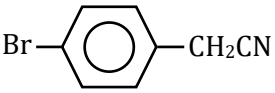
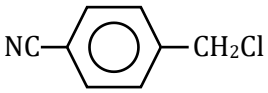
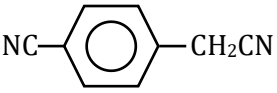
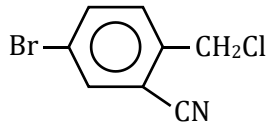
4. The product obtained in this reaction is :-



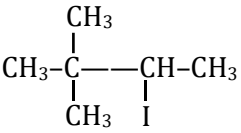
(1) 

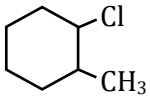
(2) 

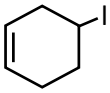
(3) 

(4) 

5. Which of the following alkyl halide undergoes rearrangement in S_N1 reaction ?

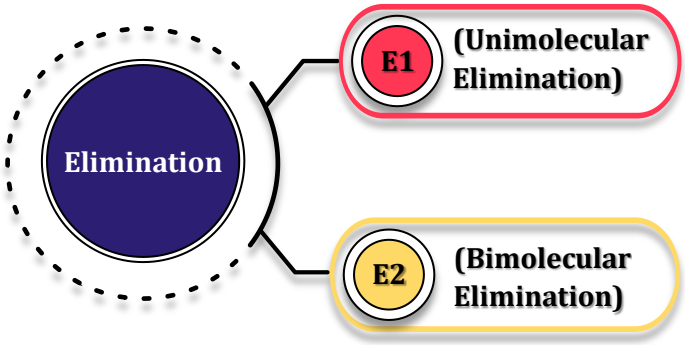
(1) 

(2) 

(3) 

(4) All of these

(ii) Elimination Reactions :

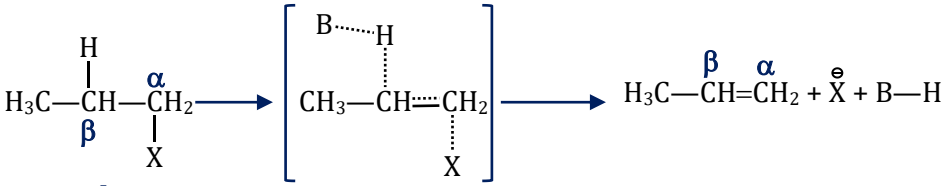


(A) Dehydrohalogenation of Halide

E2 (Bimolecular Elimination)

1. It is also known as α, β- elimination / 1,2 - elimination.

2. It is a single step reaction. No intermediate is formed.



X–Halogen
B–Base

Transition State

3. Rate = k[Alkyl halide][Base]

Order = 2

Molecularity = 2

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4. Rate of E2 $\propto$ Stability of alkene

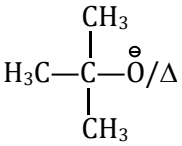
5. In rate determining step (rds), C-H and C-X bond breaking takes place.

Hence, rate of reaction will depend on the bond strength of these bonds.

6. Reagents:

Alcoholic KOH/Δ

$NaNH_2/\Delta$ (Sodamide)



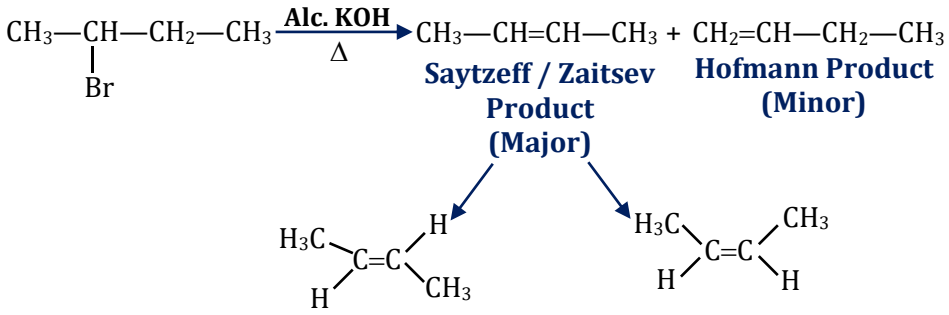
(tert-Butoxide ion/ t-BuO$^{\ominus}$ ion)

7. Stereochemistry of E2 reaction.

E2 reaction – Anti Elimination

Leaving group and β hydrogen must be anti to each other.

8.

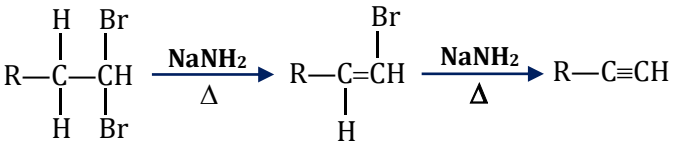


Saytzeff / Zaitsev alkene : More stable alkene

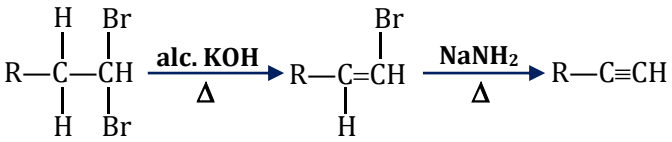
Hoffmann alkene : Less stable alkene

Note: When an alkyl halide has more than one type of β hydrogen mixture of products formed.

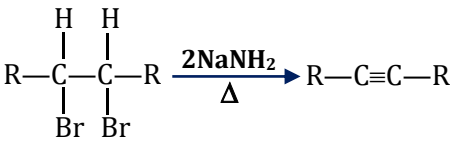
Geminal and vicinal dihalide react with $NaNH_2$ to give alkyne as major product.



Geminal dihalide



Geminal dihalide



Vicinal dihalide

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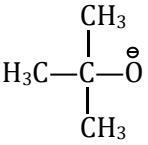
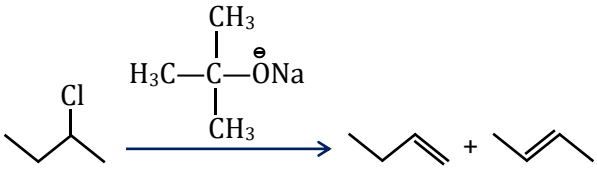
Elimination Reactions

Generally Saytzeff alkene is formed as major product but in following cases Hoffmann alkene may form as major product.

Case:1 When bulky base is present

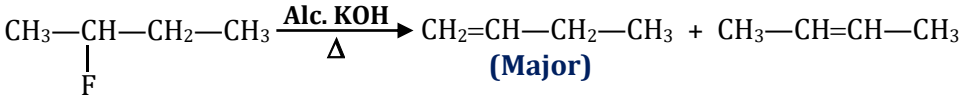
Case:2 When substrate is having poor leaving group like —F

Case: 1 When bulky base is present  **(tert-Butoxide ion)**



(Major)

Case: 2 When substrate is having poor leaving group like —F

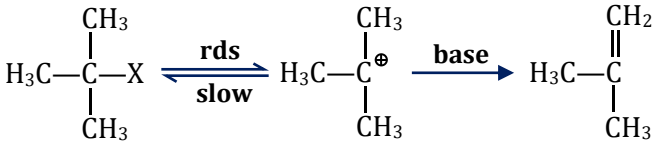


(Major)

E1 (Unimolecular Elimination)

1. It is a two step reaction.

2. Carbocation intermediate is formed. Rearrangement is possible.



X-Halogen

3. Kinetics of reaction.

Rate = k[Alkyl halide]

Order = 1

Molecularity = 1

4. Rate of E1 $\propto$ Stability of carbocation formed

5. In rate determining step (rds), C-X bond breaking takes place.

Hence, rate of reaction will depend on the bond strength of this bond.

6. Reagents:

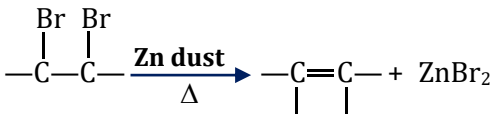
H_2O/Δ

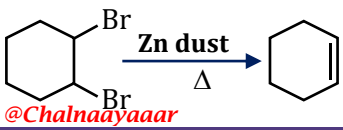
ROH/Δ

(B) Dehalogenation of vicinal dihalide

Dehalogenation is also an example of elimination(E2) reaction.

Reagent used: Zn dust/Δ





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TG: @Chalnaayaaar

(iii) Reaction with Metals :

Grignard reagent

Preparation: $R—X + Mg \xrightarrow{\text{Dry ether}} R—MgX$

Chemical reactions of R MgX

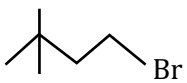
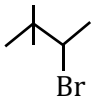
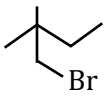
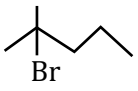
$$R—MgX + \begin{matrix} H—Cl \\ H—Br \\ H—OH \\ H—OR \\ H—OPh \\ H—NH_2 \\ H—NR_2 \\ H—O—C(=O)—R \\ \text{(cyclopentadiene)} \\ H—C\equiv C—H \end{matrix} \longrightarrow R—H + Mg(X)(Z)$$

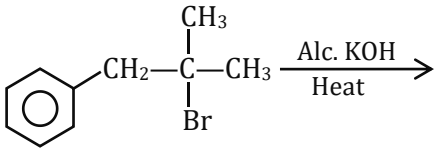
Z → Remaining part of reagent

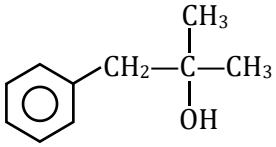
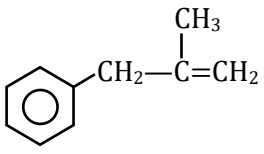
Note: Grignard reagent behaves like a base (reacts with compounds containing acidic H) as well as like a nucleophile.

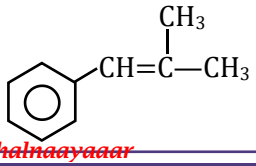
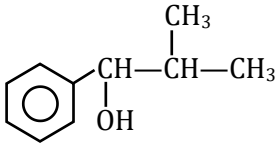
Eq. $R—Cl + RMg \xrightarrow{\text{NSR}} R—R + MgCl_2$ (product)

BEGINNER'S BOX-5

1. The reactivity of alkyl halides in E2 elimination reactions follows the order
   (1) R–I < R–Br < R–Cl < R–F (2) R–F < R–Cl < R–Br < R–I
   (3) R–I > R–Cl > R–Br < R–F (4) R–I < R–Br < R–F < R–Cl
2. Which of the following alkyl halides gives a mixture of alkenes on dehydrohalogenation?
   (1) n–Propyl halide (2) Isopropyl halide (3) s–Butyl bromide (4) t–Butyl bromide
3. Which of the following cannot undergo E2 reaction ?
   (1)  (2)  (3)  (4) 
4. What is the major product of the following reaction?



(1)  (2) 

(3)  (4) 

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5. Major product of the reaction :

$(CH_3)_3C–Cl + C_2H_5ONa \longrightarrow$

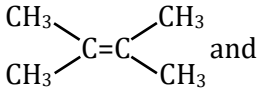
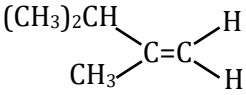
would be :-

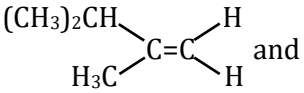
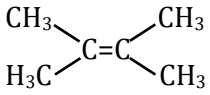
(1) $(CH_3)_3C—OC_2H_5$ (2) $(CH_3)_3C—C_2H_5$ (3) $(CH_3)_2C=CH_2$ (4) $CH_3—CH=CH—CH_3$

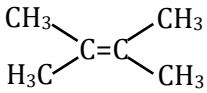
6. $CH_3—\underset{CH_3}{CH}—\underset{CH_3}{C(Br)}CH_3—$ $\xrightarrow{\overset{\ominus\oplus}{MeOK}}$ X (major)

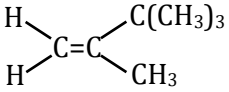
$\xrightarrow{(CH_3)_3C–\overset{\ominus\oplus}{OK}}$ Y (major)

X and Y are respectively :-

(1)  and 

(2)  and 

(3) Both 

(4) Both 

7. 1–phenyl–2–chloro propane when treated with alc. KOH mainly gives :-

(1) 1–phenyl propene (2) 3–phenyl propene

(3) 1–phenyl–2–propanol (4) 3–phenyl–1–propene

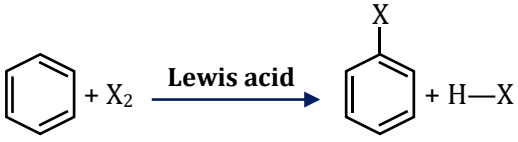
8. $CH_3–\underset{Ph}{\underset{|}{CH}}–\underset{Br}{\underset{|}{CH}}–CH_3 \xrightarrow[\Delta]{KOH}$ (A) (major) + (B) (minor) major product will be :-

(1) $CH_3–\underset{Ph}{\underset{|}{C}}=CH–CH_3$ (2) $CH_3–\underset{Ph}{\underset{|}{C}}–CH=CH_2$

(3) $CH_2=\underset{Ph}{\underset{|}{C}}–CH_2–CH_3$ (4) $CH_2=\underset{CH_3}{\underset{|}{C}}–CH_2–Ph$

Methods of Preparation of Haloarenes

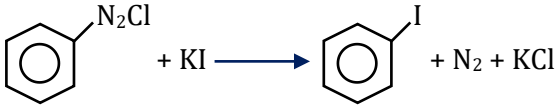
1. From aromatic hydrocarbons :



2. From benzene diazonium salt (Sandmeyer reaction) :

TG: @Chalnaayaaar

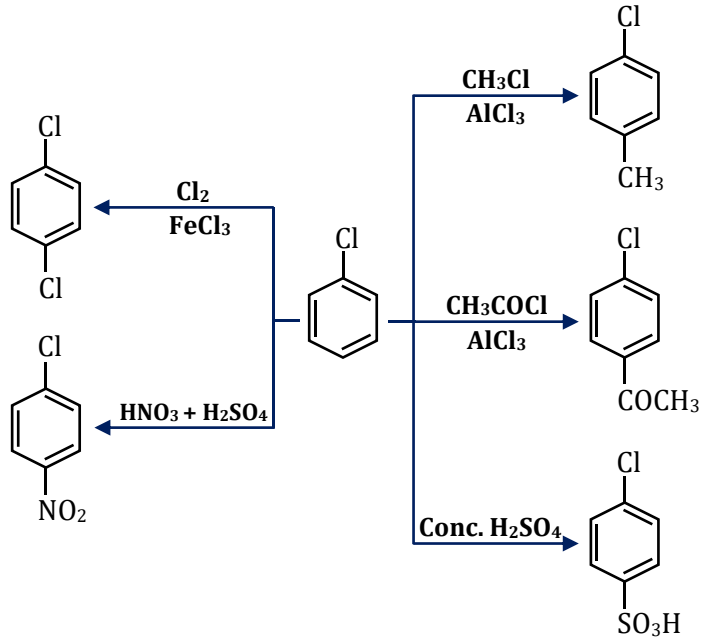
Note:



Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.

Chemical Reactions of Haloarenes

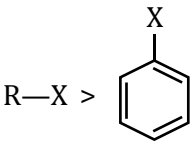
1. Electrophilic Substitution Reaction (ESR) :



2. Nucleophilic Substitution Reaction (S_NAr) :

Aryl halides are extremely less reactive towards nucleophilic substitution reaction.

Reactivity order :



Reasons :

(i) C-X bond acquires partial double bond character due to resonance. As a result bond cleavage in haloarene is difficult than haloalkane.

(ii) Difference in hybridisation of carbon atom in C-X bond. (As % 's' character increases, bond length decreases, bond strength increases.)

Nucleophilic Aromatic Substitution (S_NAr) by Addition Elimination

Nucleophilic aromatic substitution can occur when strong electron withdrawing groups are present at ortho or para position with respect to the halogen atom.

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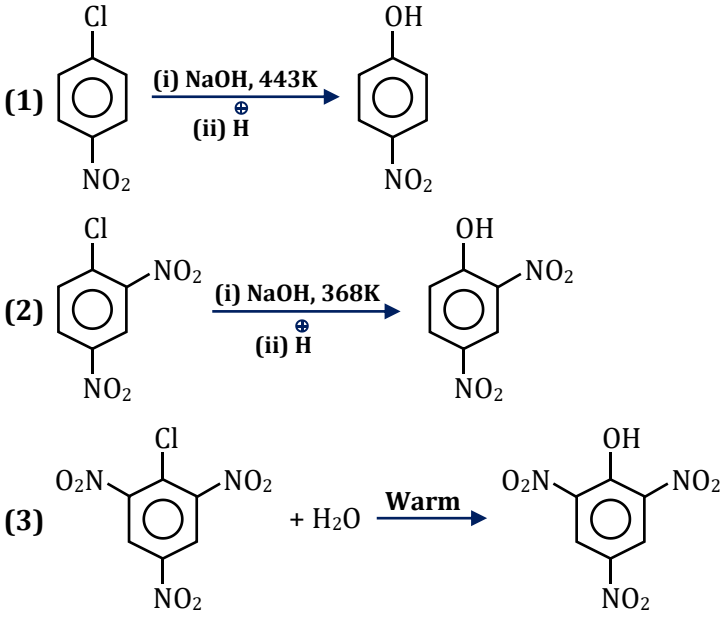
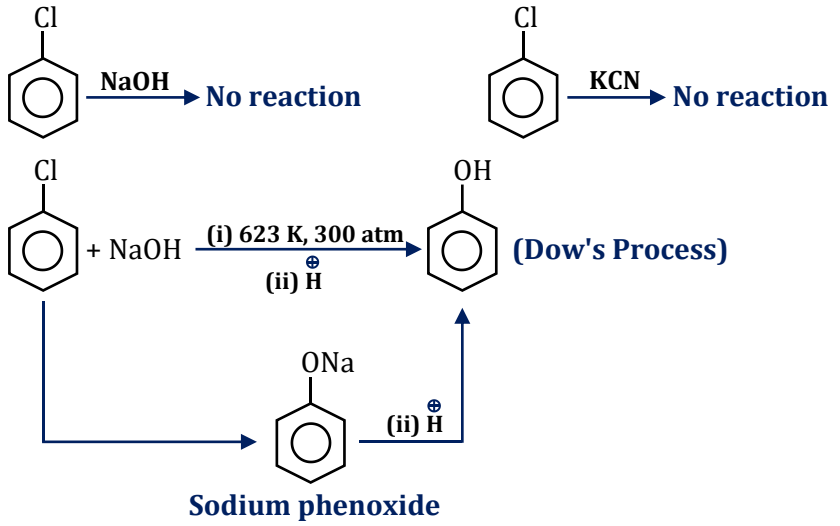


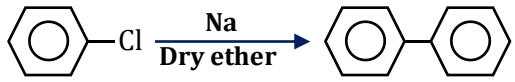
Note: Electron withdrawing groups present at ortho-para position with respect to the leaving group increases rate of reaction.

Aryl halide without electron withdrawing substituents don't react with most nucleophiles under ordinary conditions.



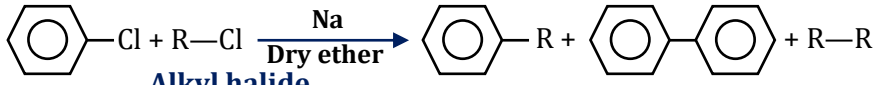
3. Reaction with metals :

Fittig Reaction



Aryl halide

Wurtz Fittig Reaction



Aryl halide **Alkyl halide** **(Major)**

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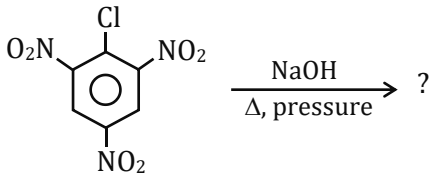
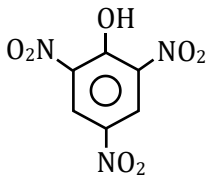
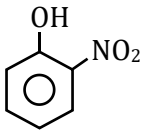
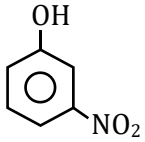
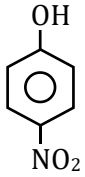
BEGINNER'S BOX-6

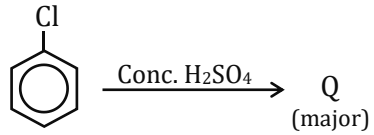
1. 

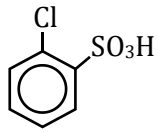
(1) 

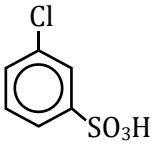
(2) 

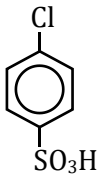
(3) 

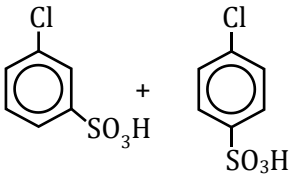
(4) 

2. 

(1) 

(2) 

(3) 

(4) 

Polyhalogen Compounds

$CHCl_3$ and CHI_3 (chloroform and iodoform) :

$CHCl_3$ (Chloroform)

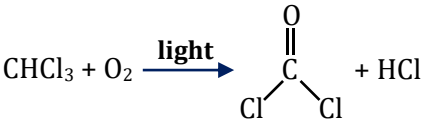
It was used as an anaesthetic.

Before being used it was tested with aq. $AgNO_3$

Pure $CHCl_3 \xrightarrow{AgNO_3}$ No reaction

Impure $CHCl_3 \xrightarrow{AgNO_3} AgCl\downarrow$

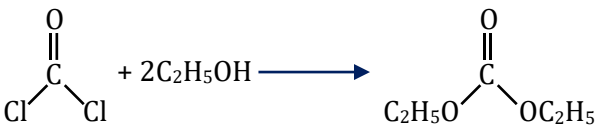
Chloroform is slowly oxidized by air in the presence of sunlight to an extremely poisonous gas 'phosgene'



Phosgene

To prevent this chloroform is stored in dark bottles and completely filled so that the air is kept out.

Small quantity of ethanol (1%) is also added



(Diethyl carbonate)

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CHI_3 (Iodoform)

It was used as an antiseptic.

$CHI_3 \xrightarrow[\text{contact}]{\text{Skin}} I_2$ (has antiseptic properties)

Pure $CHI_3 \xrightarrow{AgNO_3} AgI\downarrow$ (yellow ppt)

Freons

The chlorofluoro carbon compounds of methane and ethane are called freons.

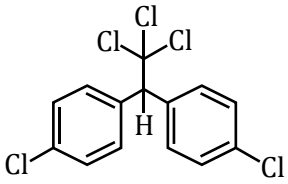
Examples: CCl_2F_2, $C_2F_4Cl_2$ etc.

They are produced for aerosol propellants, refrigeration and air conditioning purposes. Excess use results in ozone layer depletion.

DDT(p, p'-Dichlorodiphenyltrichloroethane)

Prepared by heating chloral and chlorobenzene in the presence of conc. H_2SO_4.

It was used as insecticide.



Golden Key Points

Test of $CHCl_3$

Reagent	Pure $CHCl_3$	Impure $CHCl_3$ ($COCl_2$ +HCl)
• Blue litmus	No Change	turns into red
• $AgNO_3$	No reaction	White ppt of AgCl

BEGINNER'S BOX — ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6		
	Ans.	2	1	1	1	2	2		
BEGINNER'S BOX-2	Que.	1	2	3	4	5			
	Ans.	2	2	3	3	3			
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6		
	Ans.	1	2	4	2	2	4		
BEGINNER'S BOX-4	Que.	1	2	3	4	5			
	Ans.	1	4	2	1	4			
BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7	8
	Ans.	2	3	3	3	3	1	1	1
BEGINNER'S BOX-6	Que.	1	2						
	Ans.	1	3						